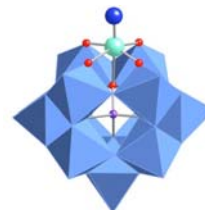
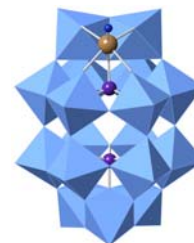


In the most recent grant period, our attention has turned to the preparations of another new class of functionalized polyoxometalates (POMs), namely those incorporating a nitrido-metal unit into the POM framework. Our first report<sup>6</sup> introduced both rhenium- and osmium-nitrido derivatives of the Keggin POM, *i.e.*  $[\text{PW}_{11}\text{O}_{39}(\text{Os}^{\text{VI}}\text{N})]^{4-}$  and  $[\text{PW}_{11}\text{O}_{39}(\text{Re}^{\text{VI}}\text{N})]^{4-}$  which have the structure shown at right. The  $[\text{PW}_{11}\text{O}_{39}(\text{Re}^{\text{VI}}\text{N})]^{4-}$  species has readily accessible one-electron oxidation and reduction potentials of +0.49 V and -0.47 V *vs.* SCE); we have observed and characterized  $[\text{PW}_{11}\text{O}_{39}(\text{Re}^{\text{V}}\text{N})]^{5-}$  as an intermediate, and have been able to prepare  $[\text{PW}_{11}\text{O}_{39}(\text{Re}^{\text{VII}}\text{N})]^{3-}$  through oxidation with  $[\text{TBA}][\text{Br}_3]$ .

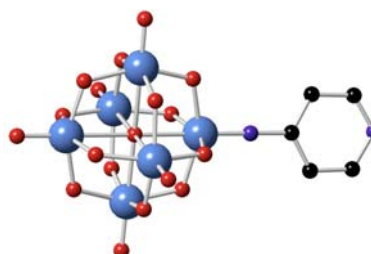
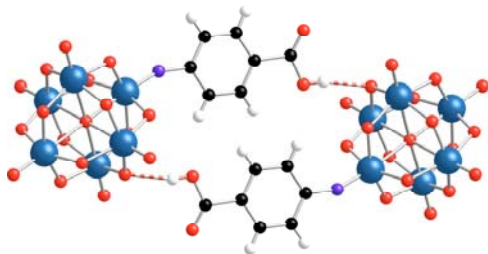


The nitrido work has progressed to include examples of corresponding Dawson POMs, such as  $[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}(\text{Os}^{\text{VI}}\text{N})]^{7-}$  (shown at right) and its analogous  $\alpha_1$ -isomer.<sup>9</sup> In this work, we have also been able to interpret and simulate the highly complex second order ESR spectrum of  $[\text{PW}_{11}\text{O}_{39}(\text{Re}^{\text{VI}}\text{N})]^{4-}$ . A complete assignment of the  $^{183}\text{W}$  NMR spectrum of  $[\text{PW}_{11}\text{O}_{39}(\text{Os}^{\text{VI}}\text{N})]^{4-}$  has been accomplished using correlation spectroscopy and in the case of  $[\alpha_2\text{-P}_2\text{W}_{17}\text{O}_{61}(\text{Os}^{\text{VI}}\text{N})]^{7-}$ , a nearly unambiguous assignment has been made using selective  $^{31}\text{P}$  decoupling techniques and an analysis of observed coupling constants.



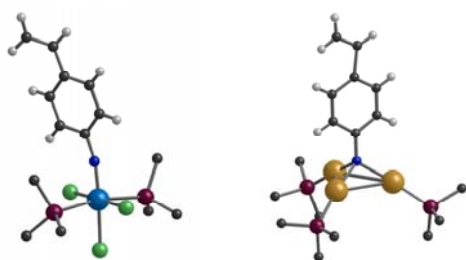
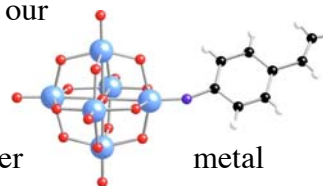
In ongoing work, we have prepared examples of Cr(V) and Mn(V) nitrido-POMs: the orange species  $[\text{PW}_{11}\text{O}_{39}(\text{Cr}^{\text{V}}\text{N})]^{5-}$  has been obtained in high yield,<sup>10</sup> while the blue Mn(V) species  $[\text{PW}_{11}\text{O}_{39}(\text{Mn}^{\text{V}}\text{N})]^{5-}$  has thus far been obtained only in small quantities via the photolysis of  $[\text{PW}_{11}\text{O}_{39}(\text{Mn}^{\text{III}}\text{N}_3)]^{5-}$ .<sup>11</sup> Preliminary GC/MS results indicate that  $[\text{PW}_{11}\text{O}_{39}(\text{Cr}^{\text{V}}\text{N})]^{5-}$  is a competent nitrogen atom transfer reagent: reaction of  $[\text{PW}_{11}\text{O}_{39}(\text{Cr}^{\text{V}}\text{N})]^{5-}$  with trifluoroacetic anhydride and cyclo-octene produces the corresponding *N*-trifluoroacetyl aziridine, although its mass spectrum indicates an association with  $[\text{Na}]^+$  (from an unknown source).<sup>10</sup>

In the area of organoimido- POMs, we continue to search for more elaborately-derivatized species capable of extending the utility of POM systems. One of our long-term goals is the development of donor-acceptor systems, based on an imido-POM coordination chemistry, that would be capable of photo-induced charge separation. In this respect, we have prepared and characterized several systems, such as the imido-benzoic<sup>12</sup> and imido-pyridyl<sup>13</sup> hexametallate species  $[\text{Mo}_6\text{O}_{18}(\text{N}-\text{C}_6\text{H}_4\text{CO}_2\text{H})]^{2-}$  and  $[\text{Mo}_6\text{O}_{18}(\text{N}-\text{C}_5\text{H}_4\text{N})]^{2-}$  whose structures as determined by single-crystal X-ray diffraction are shown below. To our disappointment, neither of these species



can presently support a coordination chemistry: the synthesis of the imido-benzoic system is plagued by poor reproducibility and low yields, while the imido-pyridyl system is not a competent Lewis base (as a result of the powerful electron-withdrawing effect of the POM unit). Strategies to circumvent these problems will be discussed below.

We continue to develop soluble polymers that incorporate POMs as covalently attached backbone substituents.<sup>4,7</sup> The prototype building block in this work is our styrylimido POM  $[\text{Mo}_6\text{O}_{18}(\text{N}-\text{C}_6\text{H}_4\text{CH}=\text{CH}_2)]^{2-}$  whose structure is shown at right. Our initial synthesis of co-polymers with styrenic monomers has now been extended to include co-polymers of various acrylic materials. We have also broadened our strategy to other systems, such as the styrylimido complexes  $[\text{Re}^{\text{V}}(\text{NAr})\text{Cl}_3(\text{PR}_3)_2]$  and  $[\{\text{Au}^{\text{I}}(\text{PR}_3)\}_3(\mu_3\text{-NAr})]^+$  whose structures<sup>14</sup> are given below. In the case of the rhenium system, we have been demonstrated the ability to perform both free-radical initiated co-polymerization with acrylates (at the styrylimido function) and ligand substitution (on the chloride and phosphine ligands). Given the near-ubiquity of organoimido complexes throughout the *d*-block metals, this approach is expected to be applicable to many species.



We are exploring the potential of the styrylimido POM  $[\text{Mo}_6\text{O}_{18}(\text{N}-\text{C}_6\text{H}_4\text{CH}=\text{CH}_2)]^{2-}$  as a platform for introducing additional functionality via metathetical exchanges at its vinyl group using Schrock and Grubbs catalysts. This styrylimido POM is especially promising for such reactions since it is accessible in high yield and its  $[\text{Mo}\equiv\text{N}]$  linkage is particularly robust.

### Impact and Relevance to DOE Interests

Although the aziridination of olefins is much less developed than the corresponding oxygen atom transfer, high-valent nitrido complexes bearing organic co-ligands have displayed significant activity. We anticipate similar reactivity from the metal nitrido fragments embedded in our POM systems, but with the added advantages of a ligand set with superior thermal and oxidative stability plus the ability to tune solubility (via counteranion exchange) for aqueous or organic media as desired.

In the realm of hybrid magnetic materials, a prominent goal is the utilization of mobile pi-electrons within an organic stack (such as those found in oligomeric TTF-type cations) to induce a long-range magnetic ordering of localized spins within an inorganic component, *i.e.* an indirect coupling mediated by  $\pi$ -*d* interactions. Our POM-based metalloligands provide a completely new avenue for accessing unusual compositions, geometries and phases of relevance to such materials.

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